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Synthetic preparation of thaumasite – several possible routes for thaumasite formation

A. Masárová[a,b,*], M. Fridrichová[b], K. Dvořák[b]

[a]*Research Institute for Building Materials, Hněvkovského 30/65, 617 00 Brno, Czech Republic*
[b]*Faculty of Civil Engineering, Brno University of Technology, Veveří 331/95, 602 00 Brno, Czech Republic*

Abstract

Presented work is a part of an experiment where limestone is partially replaced by fluidized fly ash during cement manufacturing. Hydration of this type of cement is connected to formation of AFt phases – thaumasite and ettringite that cause serious damage to cement stone. Thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) is less known and less common. It forms especially at lower temperatures. During its growth C-S-H phases are built into thaumasite unite cell, therefore, cement stone decomposes. To preclude thaumasite formation, further research of this mineral is necessary; therefore, its synthetic preparation in sufficient quality is important. The aim of this work was to verify several routes for thaumasite synthetic preparation. In the beginning, burning of mixtures prepared on stoichiometric proportions of compounds in thaumasite was done then two methods used in literature were tried and in the end a new method based on main calcium silicate phases was realized.

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Keywords: Sulfate attack; AFt phases; thaumasite; ettringite; cement; X-ray powder diffraction

1. Introduction

Nowadays, the tendencies to replace raw materials for cement production or cement itself by industrial wastes or by-products are very intense. The main reason is that the manufacturing of building materials, especially of cement, is connected to production of high amount of CO_2 emission. Blast furnace slag or fly ash are commonly used as a replacements of cement. Presented work is a part of an experiment where limestone is replaced by fluidized fly

* Corresponding author. Tel.: +420-730-519-701.
E-mail address: masarova@vustah.cz

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ash during cement manufacturing which leads to lower CO_2 emissions, even by 10 %. However, AFt phases are formed during the hydration of this type of cement and they lead to serious concrete damage. It is fundamental to study these phases properly and to find out a way how to prevent their formation in concrete or cement. This article deals especially with less known representative of Aft phases – thaumasite and describes attempts for its synthetic preparation.

Thaumasite, $CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$, is a mineral with hexagonal pyramidal structure containing SiO_4 tetrahedra and CO_3 triangular planes [1]. It has silicon in 6-coordination with hydroxyl which is very unusual [2]. Morphologically, it forms fibers and needles and it is very similar to ettringite. In cement-based materials, both thaumasite and ettringite occur as a product of sulfate attack. In the past, thaumasite sulfate attack (TSA) was often confused with classic sulfate attack (ettringite formation) because of high similarity of ettringite and thaumasite. According to several authors, these minerals create solid solution called woodfordite which leads to another confusion in their recognition [e.g. 2,3,4]. On the other hand, some methods can positively confirm thaumasite occurrence – SEM with EDX spectra, FTIR or in some cases even X-ray diffraction (XRD) [e.g. in 4,5,6].

The ambient conditions for thaumasite formation stated in literature [2,7] are:

- Temperature bellow 15 °C (ideally at between 0–5 °C)
- Source of calcium silicates – e.g. calcium oxide (hydroxide) plus silicon dioxide
- Source of sulfates – e.g. gypsum $CaSO_4 \cdot 2H_2O$, sulfates in the groundwater etc.
- Presence of carbonates – e.g. calcite $CaCO_3$ or atmospheric carbon dioxide
- Excessive amount of water

Bensted [2] described two different formation routes of thaumasite. Direct route is very slow and normally takes several months for thaumasite to be obtained in significant amount. It is formed by reaction of sulfate with carbonate, silicate and water. Source of carbonates is usually atmospheric CO_2 or CO_3^{2-} ions, sulfates can be internal or external source and silicate includes C-S-H phases from hydrated cement. Thus, damage caused by thaumasite formation is very serious – it incorporates C-S-H phases into its unit cell and cement binder collapses.

Indirect or so called woodfordite route described by Bensted in [2] arises by reaction between ettringite, silicate and carbonate in sufficient amount of water. This confirms the statement that ettringite could be a precursor of thaumasite formation. The beginning of this reaction is very slow but once thaumasite is formed, reaction rate increases. In this situation, also solid solution between ettringite and thaumasite occurs in significant amount until all reactants form thaumasite. Comparing these two, woodfordite route is much quicker than direct route. The presence of aluminate octahedral skeleton of ettringite should easier facilitate Al replacement by Si [2].

Many studies have been done about thaumasite and thaumasite sulfate attack, especially in UK after year 1998. There were found several structures attacked by thaumasite in motorway bridges. Expansion and deterioration of concrete by non-binder thaumasite was so serious that UK government convened the Thaumasite Expert Group [8]. These people studied mainly the process of thaumasite formation in hardened concrete, the damage, the influence of concrete composition etc. But several items have not been studied at all or not properly, e.g. pH stability, thermodynamical stability of thaumasite, etc. For further research it is necessary to synthetize thaumasite in significant amount and sufficient purity.

Several authors tried to prepare thaumasite via direct or indirect route. Bensted [12] prepared thaumasite by reaction of solution with SO_4^{2-} and CO_3^{2-} and C-S-H. Kollman [9] obtained thaumasite by mixing of Portland cement, $CaCO_3$ and gypsum in water at 2 °C. In the beginning ettringite was formed but after 40 days also thaumasite occurs. Other methods just repeated field processes in laboratory [e.g. 10,11].

According to Aguilera [5] thaumasite can be obtained by mixing of two solutions cooled at 5 °C. The first one is a solution of 10 % sugar with addition of CaO or $Ca(OH)_2$. The second solution contains Na_2SO_4, Na_2SiO_3 and Na_2CO_3. The advantage of this procedure is that use of sugary solution positively influences solubility of calcium and use of sodium salts instead of calcium reduces formation of undesirable products. This method was used in the experimental part of this work.

Purnell in [13] obtained thaumasite by placing of cementitious material with addition of alumina and calcium carbonate into $MgSO_4$ solution for 100 days at 5 °C. Thaumasite, ettringite or both were detected in all samples. One part of the experimental work described in this article is inspired by Purnell´s experiment.

In the beginning of experimental process, it was decided to try preparation of thaumasite by hydration of burned mixture designed exactly on stoichiometric proportions of CaO, SiO_2, CO_3^{2-} and SO_4^{2-} in thaumasite. This led only to a partial success. Then thaumasite was tried to prepare by methods mentioned above. Expected results were not obtained, too. The last part of the experimental work described in this paper presents thaumasite preparation from main calcium silicate phases.

2. Materials and methods

2.1. Thaumasite preparation by burning of $CaCO_3$ - $CaSO_4 \cdot 2H_2O$ – SiO_2 mixtures

The first step in thaumasite preparation was done by burning of mixtures designed on stoichiometric proportions in thaumasite, consisting of three components – calcium carbonate $CaCO_3$ p.a., chemical gypsum $CaSO_4 \cdot 2H_2O$ with 98.6% purity and silica fume SiO_2 with 96% purity. Burning was realized in high temperature chamber of X-ray diffractometer Panalytical Empyrean with Cu-Kα anode up to temperatures 600 °C, 800 °C, 900 °C and 1100 °C. After that, burning was repeated in laboratory corundum furnace up to temperatures 1000 °C and 1200 °C with isothermal stamina 5 hours in bigger amount. The temperature rise was 100 °C/min. According to results from the first burning, also the atmosphere in furnace was changed by addition of crucible with gypsum which provided SO_2 vapor. Mixtures were then analyzed by XRD. Composition of mixtures is shown in Table 1.

Table 1. Composition of mixtures designed on stoichiometric proportions in thaumasite.

Mixture	Composition (*mol*)		
	$CaCO_3$	SiO_2	$CaSO_4 \cdot 2H_2O$
A1	2	1	1
A2	4	1	1
A3	6	1	1

2.2. Thaumasite preparation from cementitious materials

Second step in attempt for thaumasite synthesis was inspired by experiment made by Purnell [13]. Synthetic monoclinic alite and belite were mixed with calcium carbonate and alumina in amounts stated in Table 2. The mixtures underwent 7 days hydration process and then they were grounded and mixed with particular amount of $MgSO_4$ solution – 30 ml for each 1 g of sample. Solutions were then maintained at temperature 5 °C to 7 °C in refrigerant device. Samples were analyzed by XRD performed on Bruker D8 Advance apparatus with Cu anode and variable divergence slits at Θ-Θ reflexion Bragg-Brentano para focusing geometry.

Table 2. Composition of mixtures for thaumasite preparation from cementitious materials.

Mixture	Composition (*g*)			
	C_3S	β-C_2S	$CaCO_3$	Al_2O_3
B1	0.50	0.50	1.00	0.00
B2	0.50	0.50	1.00	0.01
B3	0.50	0.50	1.00	0.02

2.3. Thaumasite preparation in sugary solution

Stuble [14] reported his thaumasite synthesis from chilled solutions of sugar and other compounds. His method was slightly changed by Aguilera [5]. In our experiment, we decided to prepare solutions according to this modified process.

At first, the sugar solution with concentration of 10 % was prepared and pre-cooled to 5 °C. Amount of solution was divided by mass in two bottles. Into the first part CaO was added and into the second part Na_2SO_4, Na_2SiO_3 and Na_2CO_3 were added. Mixtures were cooled another 24 hours and then mixed together. In Table 3, five resulting solutions are shown, which differ in concentration of oxides. Mixtures were placed into device with temperature 5–7 °C and tested by XRD (performed on Bruker D8 Advance apparatus with Cu anode and variable divergence slits at Θ-Θ reflexion Bragg-Brentano para focusing geometry) at particular intervals.

Table 3. Composition of mixtures for thaumasite preparation in sugary solution.

Mixture	Composition (mol/dm^3)			
	CaO	Na_2SiO_3	Na_2SO_4	Na_2CO_3
C1	0.030	0.033	0.033	0.033
C2	0.050	0.010	0.010	0.017
C3	0.050	0.017	0.010	0.017
C4	0.025	0.006	0.008	0.010
C5	0.025	0.006	0.006	0.010

2.4. Thaumasite preparation from main calcium silicate phases

According to results of previous tests, it was decided to try also thaumasite preparation from main calcium silicate phases – alite C_3S, belite C_2S and wollastonite CS in carbonic acid. The similar method was not found in literature, therefore, it still could be plausible method for thaumasite preparation.

Belite and wollastonite of sufficient quality were already available in our institute but it was necessary to prepare alite. The burning was done according to procedure known and used in Research Institute for Building Materials. The purity of alite was 99.1%.

All these minerals were grounded in vibrating mill and homogenized with other substances so stoichiometric proportions in thaumasite were achieved. Tree different materials mixtures shown in Table 4 were prepared. Solution of carbonic acid was prepared by siphon bottle with CO_2 filler where distilled pre-cooled water was added. Low temperature increases CO_2 solubility in water, therefore, higher concentration of carbonic acid is achieved. Mixtures were then placed into bottles with CO_2 water, maintained at temperature 5–7 °C and tested by XRD analysis (performed on Bruker D8 Advance apparatus with Cu anode and variable divergence slits at Θ-Θ reflexion Bragg-Brentano para focusing geometry) every 28 days.

Table 4. Composition of mixtures for thaumasite preparation from main calcium silicate phases.

Mixture	Composition (*mol*)					
	C_3S	C_2S	CS	$CaSO_4{\cdot}2H_2O$	CaO	SiO_2
D1	2	-	-	3	-	1
D2	-	1	-	1	-	-
D3	-	-	1	1	1	-

3. Results and discussion

3.1. Thaumasite preparation by burning of $CaCO_3$ - $CaSO_4{\cdot}2H_2O$ - SiO_2 mixtures

Mixed and homogenized samples were, at first, burned in high temperature chamber of X-ray diffractometer by temperature mode described above. The results of this first step were surprising because of mineral ternesite found in sample A1. Ternesite $4CaO{\cdot}2SiO_2{\cdot}CaSO_4$ is rare and unusual mineral. Its natural equivalent was described by Irran in [15] in 1997 but synthetic ternesite was mentioned in literature much sooner. In 1960 Sundius and Peterson [16] observed ternesite in green sulfate rings in cement rotary kiln as a coloring component. Its crystal

system is orthorhombic; the color is green (in case of synthetic ternesite). According to Gutt and Smith [17] ternesite is formed at temperature above 1000 °C and decomposes at 1150 °C in an open system and at about 1300 °C in closed crucibles.

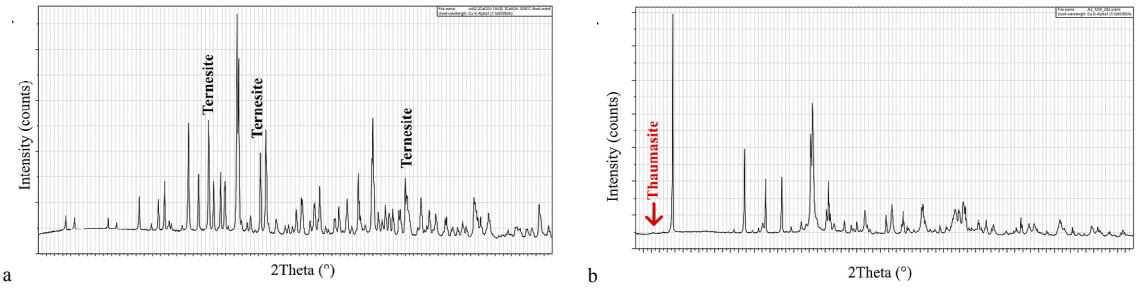

Fig. 1. (a) Diffractogram of the sample A2 burned to 1200 °C – lines with highest intensity belong to ternesite and are marked, other peaks mainly belong to anhydrite II; (b) Diffractogram of the sample A3 burned to 1200 °C after 28 days of hydration – small peak at d_{hkl} = 9.59 Å (main diffraction line of thaumasite) is labeled.

After observations made on sample A1, it was decided to change burning process, as stated above, rising from assumption that ternesite could represent in some way an equivalent of yeelimite during ettringite preparation. Ternesite was then presented in all burned samples together with anhydrite II and lime, although, the most convenient results showed sample A2. It contained quite high amount of ternesite with no residual CaO but also unreacted anhydrite II. Diffractogram of the sample A2 burned to 1200 °C is shown in Fig. 1 (a).

All samples underwent hydration process. Main product in every sample was gypsum. In samples from series A3, also portlandite occurs. After 28 days of hydration in the sample A3 burned to 1200 °C, a small peak occurs at d_{hkl} = 9.59 Å. This d value is consistent with main diffraction line of thaumasite (see Fig. 1 (b)).

3.2. Thaumasite preparation from cementitious materials

Samples were tested by XRD analysis every 28 days for 9 months. In all samples calcite, gypsum, alumina, brucite and some alite or belite were observed. High amount of amorphous phase was also identified. Even after so long period no thaumasite (or ettringite) was detected unlike in [13]. This negative result leads to a lot of questions. Sulfate solution used in experiment was $MgSO_4$ that is considered by several authors [2,18,19] to be the worst for deterioration of cement or concrete by thaumasite formation. Used materials were pure and reactive, their quality was tested before the experiment. Only one reason seems to be real. Clinker minerals might not be hydrated properly and cold environment could be the reason for stopping their hydration – therefore, convenient conditions for thaumasite formation were not presented.

3.3. Thaumasite preparation in sugary solution

Similarly to method mentioned above, samples were tested every 28 day for 9 months. Samples contained mainly an amorphous phase and calcite. They also contained monohydrocalcite ($CaCO_3 \cdot H_2O$), as a reaction product between calcite and water. Neither thaumasite nor ettringite was detected. Test method was inspired by Stuble [14] and Aguilera [5]. Concentration of solutions and also test procedure was kept. Both authors mention the presence of thaumasite in samples after few months. However, they used FTIR for detection of presented phases. It might be possible that because of huge amount of amorphous phase in our samples, thaumasite or ettringite peaks were hidden and therefore not detected by this method.

3.4. Thaumasite preparation from main calcium silicate phases

Testing of samples D2 and D3 were done by XRD analysis after 1, 4, 7, 14, 40 days, 2, 3, 4 and 5 months. Sample D1 was prepared later, so it was tested after 1, 7, 14, 28 and 56 days.

Sample D1 based on alite C_3S contained mainly gypsum, quartz and portlandite, residuum of unhydrated alite was detected in smaller amount. Also amorphous phase was visible. After 28 days of exposition, small peak appeared around d_{hkl} = 9.7 Å, which most probably belong to ettringite. After 56 days, this peak´s intensity slightly increased and a very small peak appeared next to it, at around d_{hkl} = 9.6 Å, at the main diffraction line of thaumasite. However, thaumasite presence will be confirmed by later measurements. Zoom of these peaks in shown in Fig. 2 (a).

Sample D2 based on belite phase β-C_2S contained mainly gypsum and belite, which amount decreased with time of exposition. Also calcite and very small peaks of anhydrite were detected. Samples also contained quite significant amount of amorphous phase. No thaumasite or ettringite were detected by this time.

Sample D3 based on wollastonite CS contained mainly gypsum and wollastonite. Calcite, portlandite and quartz were presented from the first day, too. The amount of amorphous phase was not obvious in this sample-series. The measurement done after 40 days of exposition showed small, almost doubled, peaks at d_{hkl} = 9.72 Å and d_{hkl} = 9.59 Å, whereas the first correspond to main peak of ettringite and the second correspond to main peak of thaumasite. With time the intensity of ettringite peak decreased in favor of thaumasite peak. In sample measurement done after 5 months, only thaumasite is presented. Fig. 3 and 4 shows details of diffractograms of this sample after 40 days (when thaumasite and ettringite were first detected) and after 5 months (where only thaumasite was observed). The zoom of ettringite-thaumasite peak in measurements done after 40 days, 3 months and 5 months is shown in Fig. 2 (b).

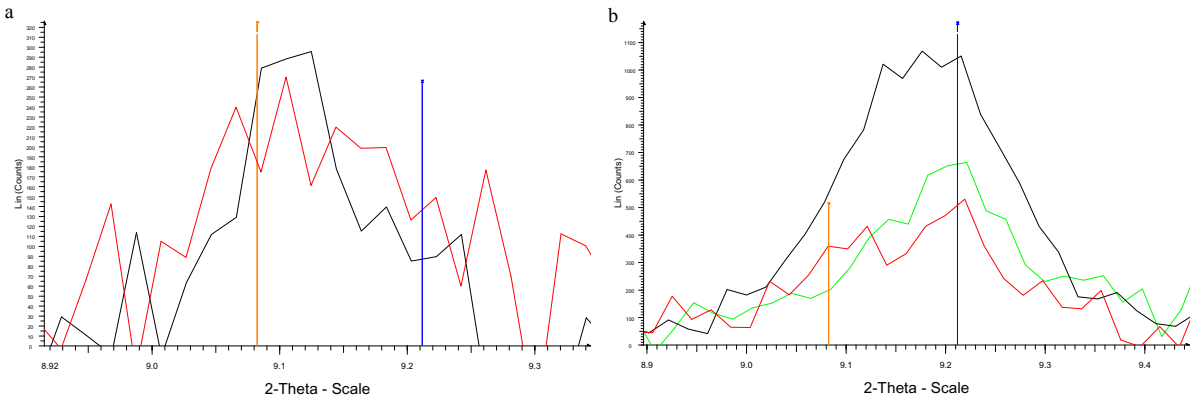

Fig. 2. (a) The zoom of ettringite – thaumasite peak in sample-series D1: red scan – measurement after 28 days, black scan – measurement after 56 days, orange line – ettringite main diffraction line, blue line – thaumasite main diffraction line; (b) The zoom of ettringite – thaumasite peak in sample-series D3: red scan – measurement after 40 days, green scan – measurement after 3 months, black scan – measurement after 5 months, orange line – ettringite main diffraction line, blue line – thaumasite main diffraction line.

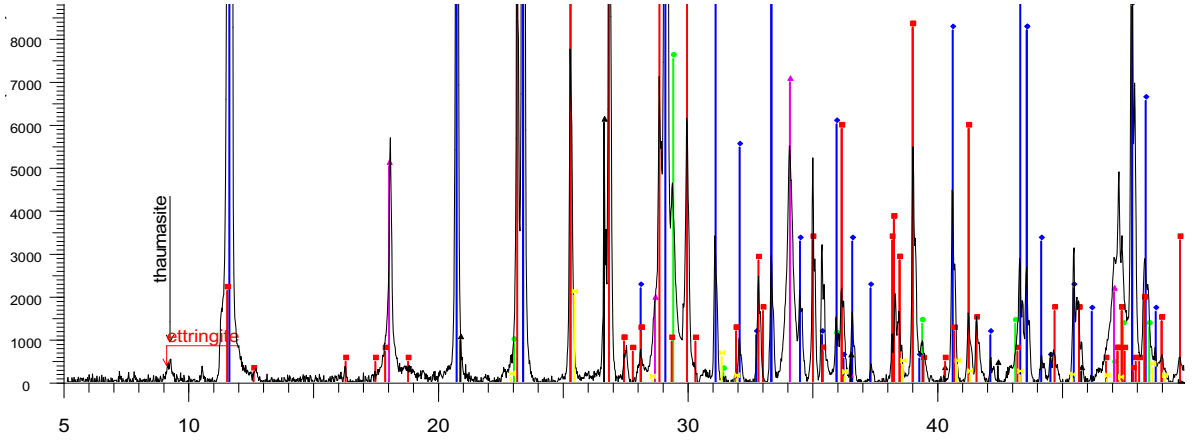

Fig. 3. Detail of the diffractogram of sample D3 scanned after 40 days of exposition: blue line – gypsum; red line – wollastonite; green line – calcite; pink line – portlandite; yellow line – anhydrite; black line – quartz.

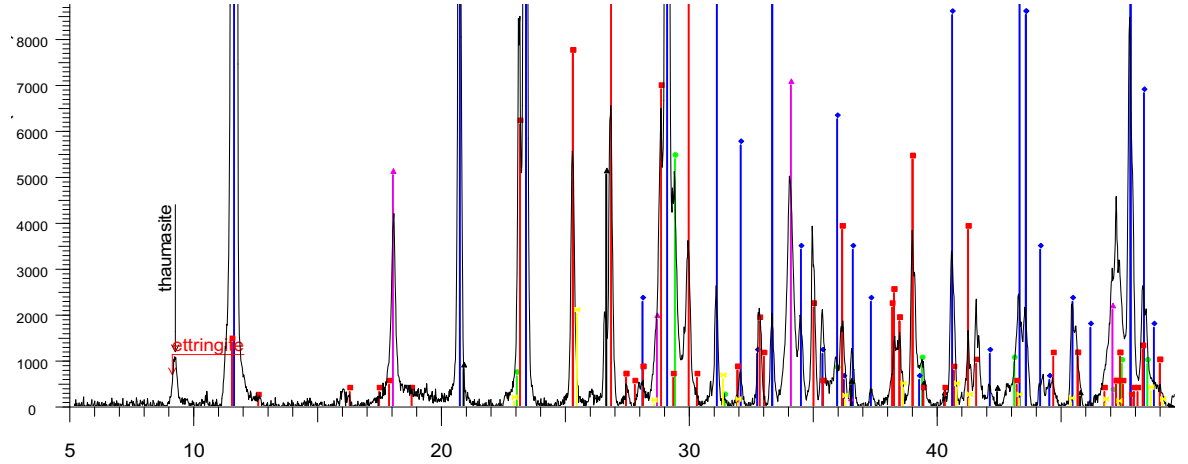

Fig. 4. Detail of the diffractogram of sample D3 scanned after 5 months of exposition: blue line – gypsum; red line – wollastonite; green line – calcite; pink line – portlandite; yellow line – anhydrite; black line – quartz.

4. Conclusions

Several possible routes for thaumasite synthetic preparation were tried. Some of them turned out to be plausible and some not. The first route described in this article was throughout burning of mixtures prepared on stoichiometric composition in thaumasite. In testing samples, mineral ternesite was found. It was assumed that ternesite could represent an equivalent of yeelimite, which hydration leads to ettringite formation. Samples were therefore allowed to hydrate. A tiny peak at d_{hkl} = 9.59 Å was observed at sample A3 burning to 1200 °C. This *d* value corresponds to main diffraction line of thaumasite. Observations made by this experiment were surprising and unexpected but they showed that this route for thaumasite preparation is plausible. The experiment described here will be extended. Ternesite hydration process need to be studied and thaumasite formation by this route will be verified.

Another two routes for thaumasite formation – from cementitious materials and by Stuble´s method, were not successful despite the fact that in literature [5,13,14] both are described like quite fast and reliable. Possible reasons of failure will be studied furthermore, some experiments might be repeated and supplemented by other testing

procedures. The last path that might lead to thaumasite formation was done by hydration of calcium silicate phases in presence of CO_2. In two of three testing samples, thaumasite or ettringite were found after one month. The sample based on alite probably contained ettringite and presence of thaumasite needs to be verified in following experiments. In the sample based on wollastonite, both ettringite and thaumasite were observed, whereas after 5 months of hydration ettringite probably disappeared and amount of thaumasite increased. Very unexpected result is that thaumasite is formed from the sample where only almost non-hydraulic wollastonite was presented. Literature states that thaumasite needs for its formation C-S-H phases which are products of hydration of hydraulic minerals [2]. This phenomenon will be studied furthermore, along with a mechanism of thaumasite formation in these samples.

Generally, the last described route of thaumasite preparation is very plausible, thaumasite was observed after short time and it seems to be stable in the environment. Samples will be studied more in following months and also other experiments will be proposed.

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